PROCESS-OIL CHARACTERISTICS IN INTEGRATED TWO-STAGE LIQUEFACTION (ITSL): COMPARISON OF PDU AND PILOT-PLANT OPERATIONS WITH BITUMINOUS COAL

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ABSTRACT

Recycle and other process oils taken during Integrated Two-Stage Liquefaction (ITSL) operations of Lummus' 30 lb/h process development unit (PDU) and the Wilsonville, AL, pilot plant (200 lb/h) were analyzed to compare the two ITSL operations. Samples were obtained from Lummus PDU Runs 3LCF7 (Indiana 5 coal), 3LCF8 and 3LCF9 (Illinois 6 coal), and Wilsonville pilot plant Run 242 (Illinois 6 coal). The process oils from pilot plant Run 242 are significantly different from the corresponding process oils from the Lummus PDU, although both were ITSL operations. Much of the difference may be ascribed to differences between the first-stage (thermal) severities and the selectivities of the deashing operations. Characteristics of the start-up solvents may also have influenced this comparison. Laboratory experiments showed that the second-stage residual feed to pilot plant run 242 was significantly less reactive toward conversion to distillate than the corresponding material from PDU Run 3LCF9 at thermal/donor, i.e., non-catalytic conditions, consistent with the process oil analysis.

INTRODUCTION

Wilsonville Run 242 is generally considered to have successfully demonstrated a scale-up of the Integrated Two-Stage Liquefaction (ITSL) process from the 0.35 ton/day process development unit (PDU) scale as operated by the Lummus Co. to the 2.5 ton/day pilot plant scale. The PDU and pilot plant have similar, though not identical, configurations. Two major differences are the interstage deasher and the second-stage hydrotreater. Lummus uses antisolvent deashing (ASDA) and a three-reactor train LC-Finer unit. Wilsonville uses critical solvent deashing (CSD) and a single-reactor H-Oil unit.

Many direct comparisons of the performances of the pilot plant and PDU cannot be made because of the lack of a uniform analytical scheme. Most notably, the distillation used to determine "resid" differs between the two operations; Wilsonville uses a 975°F (1) end point and Lummus uses an 850°F end point (2). Such parameters as resid space velocity and resid conversion, therefore, are not uniformly determined at the two plants. One of our objectives in this work was to analyze a large suite of comparable samples from the two plants, using an identical analytical scheme, to permit direct comparisons of process-oil characteristics and other derived parameters.

We analyzed several hundred samples of recycle oils and other process streams from Lummus Runs 3LCF7, 3LCF8 and 3LCF9 and daily process-oil samples from Wilsonville Run 242. In each case, the catalyst was Shell 324M (Ni/Mo on alumina) and the feed coal was Burning Star mine Illinois 6 (Run 3LCF7 used Indiana 5). The large number of samples studied has enabled us to describe "typical" compositions, to discern effects of process variables and to describe long-term trends. This paper presents a comparison of the Wilsonville and Lummus ITSL results based on our analysis of process-oil samples.

The set of Wilsonville Run 242 samples we obtained included 121 samples of V-1064 (second-stage feed), V-1067 (second-stage flashed bottoms product, recycle to first stage), T-102 bottoms (first-stage product vacuum bottoms, feed to CSD), and V-178 (first-stage heavy distillate product, second-stage distillate feed). Run 242 was two months long. Runs 3LCF7 and 3LCF9 were each nearly one year long. Run 3LCF8 was five months long. Analyses included distillation, solvent fractionation, H-NMR, phenolic determinations and microautoclave extractions.

This paper will demonstrate first that the characteristics of the process oils from Wilsonville Run 242 were relatively constant, then that the oils differed significantly from those produced in the PDU. Causes of these differences will be suggested. Finally, the results of a set of batch experiments will be presented that demonstrate an inherent difference in "thermal" reactivities of the 850°F$^+$ resids from the two operations.

Complete descriptions of the subject liquefaction runs have been published: Wilsonville Run 242 (1), and Lummus Runs 3LCF9 (2,3), 3LCF8 (2) and 3LCF7 (2). Our complete analytical data have also been reported in References 4, 5, 6 and 7, respectively.

DISCUSSION

RUN 242 - PROCESS OIL CHARACTERISTICS RELATIVELY CONSTANT

Resid Content in Process Oils Increased Slightly with Time

The 850°F$^+$ resid content of both the feed and product of the hydrotreater generally increased as Run 242 progressed. There were three periods of relatively constant resid content as shown below:

Date, 1982-83	Wt % 850°F$^+$ in Sample, Average V-1064	V-1067
12/03 - 12/16	57.4	51.8
12/18 - 12/29	63.6	58.5
01/07 - 01/21	66.6	60.1

The step increase in resid content on 12/17 was an intentional change made by the plant operators to reduce resid inventory (1).

Distillate Composition Nearly Constant - Run 242

Though the absolute amount of distillate in lbs/hr and the proportion of distillate in any stream did change with time in Run 242, the compositions of the 850°F$^-$ process oil distillates were remarkably steady after 11/28/82. The proton distributions of the V-1064 and V-1067 distillates and the V-178 samples showed little change over the course of the run; in fact, the calculated standard deviations approach our experimental reproducibility (8). This indicates 1) that the hydrogen content of these distillates is nearly constant, and 2) that the donor-solvent quality of the distillates is also nearly constant. This was confirmed by the donor solvent quality as measured by microautoclave tests, which was nearly constant for each type of process oil tested.

Resid Composition Fairly Constant

As noted above, the resid content in the various process streams increased in a step-wise fashion with time in Run 242. However, the compositions of the first-

stage product resid (T-102 bottoms) and the second-stage feed resid (V-1064) were fairly constant as measured by solvent fractionation. The scatter in the solvent fractionation data for these samples was certainly greater than experimental uncertainty, but there is no obvious trend to the data.(4) The proton distributions of the samples from these two streams may show some increase in aromaticities as the run progressed.(4) This may be a result of the recycle of hydrotreater product which showed a relatively large increase in aromaticity with time, as discussed below.

As with the hydrotreater feed resids, the HTR product resid (V-1067) compositions showed no trend as measured by solvent fractionation data. However, the aromaticity of the HTR product resid increased from about 18 to 25% over the course of the run. This indicates decreasing hydrogenation of the resids which may result partially from the increasing hydrotreater temperature. Higher temperature is thermodynamically unfavorable to hydrogenation. It appears likely that there was an additional cause, perhaps catalyst deactivation, because the decrease was fairly continuous whereas temperatures were increased in steps.

EFFECT OF CSD ON RESID COMPOSITION

In Run 242 the CSD unit removed solids from the first-stage product resid to prepare the second-stage feed resid. The T-102 bottoms (pilot plant distilled first-stage product resid) are about 89% THF soluble and contain nearly equal levels of IOM and ash. After CSD processing, the IOM and ash levels are generally reduced to well below 0.5% of the non-distillate second-stage feed. Other than removing solids, the CSD unit also tends to selectively reject the preasphaltenes fraction of the soluble resid. This is clearly seen by comparing the compositions of the second-stage feed soluble resid and the first-stage product soluble resid which are summarized below:

Resid Sample	Average wt % of THF-Soluble Resid		
	Oils	Asphaltenes	Preasphaltenes
First-stage product (T-102 Bottoms)	51	22	27
Second-stage feed (V-1067)	56	25	19

This selective fractionation of the resid may well be important to the performance of the second stage.

LUMMUS AND RUN 242 PROCESS OILS VERY DIFFERENT

It was demonstrated above that many Run 242 process-oil characteristics were relatively invariant over the course of the run. This is not usually the case in the Lummus PDU runs. That plant has been used to investigate a large number of variables. Commonly, seven or more first-stage "runs" and perhaps ten deasher "runs" are made for every second-stage "run". Also, modes of recycle are sometimes changed. Consequently, the compositions of the process oils undergo discontinuous changes.

Some of the text that follows presents comparisons of data from Run 242 and various Lummus PDU runs. Complete data are available in our reports on Wilsonville Run 242 (4) and Lummus Runs 3LCF7 (7), 3LCF8 (6) and 3LCF9 (5). For the sake of brevity, many comparisons will be made based on average values. Because averages are not always meaningful without knowledge of the distribution of the individual data, we have included standard deviations and sometimes a range of data for many of the averages.

Resid Quality in Run 242 Superior to Lummus Runs/Deashing Differences

One major difference between the practice of ITSL at the PDU (Lummus) and the pilot plant (Wilsonville) is the interstage deashing process. The critical solvent deashing (CSD) process employed at Wilsonville selectively rejects a portion of the preasphaltene fraction of the soluble resid as demonstrated above. On the other hand, our analyses of twenty-six Lummus antisolvent deasher (ASDA) runs with bituminous coal products demonstrated no consistent fractionation of the THF-soluble resid (5, 6, 7). This is certainly one reason (out of perhaps several) that the second stage feed resid contained fewer preasphaltenes in Run 242 than in typical Lummus operations. Since resid is recycled around the entire integrated process, each resid stream from Run 242 had relatively fewer preasphaltenes than the correspondong resid sample from Lummus runs. As a general rule, preasphaltenes are less hydrogenated than benzene solubles. As expected, therefore, Run 242 resids were lower in aromaticity than typical Lummus resids.

Soluble Resid Sample	Run #	Average Value ± Std Dev wt % Preasphaltenes	H-Aromaticity, %
Second-stage feed	242	19 ± 2	34 ± 2
	3LCF7	43 ± 4	-
	3LCF8	36 ± 5	44 ± 3
	3LCF9	35 ± 5	47 ± 3
Second-stage product	242	13 ± 3	22 ± 3
	3LCF7	28 ± 6	-
	3LCF8	23 ± 6	30 ± 5
	3LCF9	22 ± 4	37 ± 6

For both units, the resids are upgraded, i.e., preasphaltenes and aromaticity are reduced, in the second stage. However, these data also demonstrate the significant difference in resid compositions for Run 242 and the Lummus runs. Both aromaticities and preasphaltene contents differ from one unit to the other by at least two standard deviations. This may have a significant bearing on process performance, e.g., second-stage conversion. It is expected that preasphaltenes may react kinetically differently than asphaltenes and residual oils and may require more hydrogen and produce more hetero-gases upon upgrading to equivalent products. Additionally, resids of different solubility characteristics and hydrogen contents may deactivate the catalyst at different rates.

In Run 242, the CSD unit consistently reduced the solids (IOM and ash) concentration in the second-stage feed to less than 0.5% (4). The Lummus runs all operated on feeds containing significant levels of solids (IOM plus ash) as shown below.

ITSL Run No.	Solids Concentration in Second-Stage Feed wt %, Average (Range)
242	0.1 (<0.1 - 0.6)
3LCF7	8 (1 - 17)
3LCF8	8 (1 - 11)
3LCF9; deashed	5 (1 - 12)
3LCF9; non-deashed	12 (5 - 17)

These solids are typically composed of two parts IOM and one part ash. The high solids contents in the Lummus feeds result from periods during which the deasher was not operating at full efficiency or was bypassed. Once the solids entered the feed tank, they purged out slowly.

Solids concentration may also have significant bearing on process performance, both mechanically (e.g., deposits, erosion or viscosity problems) and chemically (e.g., second-stage conversion). Metals may deposit on catalyst surfaces and cause deactivation.

Process Streams Contain More Resid in Run 242 than in Lummus Runs

The hydrotreater feed in Run 242 contained a somewhat greater resid (lower distillate) concentration than for typical Lummus second-stage feeds as shown below.

Run No.	$850°F^+$ Content of Second-Stage Feed, wt %, range
242	57 - 67
3LCF7	52 - 75
3LCF8	50 - 61
3LCF9	45 - 63

As discussed earlier, the Run 242 $850°F^+$ resids were essentially ash-free whereas the Lummus resids contained significant amounts of ash. Therefore, the difference in ash-free resid content is even greater than shown in the above table.

Distillate Process Oil Comparison

The following table compares the compositions of the second-stage $850°F^-$ distillates from Run 242 and from several Lummus ITSL runs in terms of proton distributions and microautoclave extractions. The microautoclave tests were all performed at our modified equilibrium conditions which are designed such that donor concentration is the limiting factor in coal conversion (7).

		Average Value		
$850°F^-$ Sample	Run	H Aromaticity % (Range)	Cyclic / Alkyl H	Microautoclave Conversion wt % MAF Coal ± Std Dev
Second-stage feed	242	17.4 (17-20)	0.64	70 ± 1
	3LCF7	40.2 (31-50)	0.98	-
	3LCF8	40.8 (35-48)	1.07	78 ± 7
	3LCF9	38.3 (34-47)	1.04	83 ± 6
Second-stage product	242	11.3 (10-12)	0.68	83 ± 1
	3LCF7	17.3 (11-28)	0.98	-
	3LCF8	18.0 (17-20)	1.07	90 ± 2
	3LCF9	22.9 (18-33)	1.01	89 ± 2

Aromaticity relates inversely to hydrogen content. The ratio of cyclic to alkyl aliphatic protons at constant aromaticity correlates with donor solvent quality (9)

and relates inversely to paraffin content. The increase in hydrogen content (decreased aromaticity) and donor solvent quality between the second-stage feed and product distillates is evident for all these runs. However, the Run 242 distillates are significantly different from those produced in the Lummus PDU. Although the compositions of the Lummus distillates spanned a fairly broad range, the Wilsonville distillate compositions were considerably outside that range.

A GC/MS investigation of these oils revealed that the Run 242 distillates are much more complex because of extensive alkyl substitution on aromatic rings and contain considerably greater concentrations of paraffins relative to most Lummus samples from equivalent process streams. This is consistent with the ^{1}H-NMR and micro-autoclave data. The Run 242 distillates are more highly hydrogenated but a lower proportion of the hydrogen is found in the desirable hydroaromatic form.

Elemental analyses obtained at Lummus and supplied by Mr. M. Peluso confirm the difference in hydrogen content for various ASTM D-1160 boiling cuts:

	H/C Atomic Ratio	
Boiling Fraction	3LCF9 Product	Run 242 V-1067 12/10/82
500 x 650°F	1.40	1.50
650 x 850°F	1.16	1.38
850°F^{+}	0.86	1.04

One potential cause of the observed differences in distillate oils is the effect of the different start-up oils used in the Wilsonville and Lummus programs. Lummus uses creosote oil/hydrogenated creosote oil as a start-up solvent. Run 242 used solvent produced from prior runs (1). Hydrogenated creosote oil is relatively aromatic, non-alkylated and non-paraffinic compared to most coal liquids and is an excellent donor solvent. An exhaustively recycled oil might be expected to be relatively paraffinic and alkylated (9). The solvents from each plant appear to retain certain characteristics of their respective start-up oils long after start-up. This could indicate inefficient solvent turn-over or perhaps it could be an example of multiple steady states (10).

RUN 242 - GREATER SCT SEVERITY AND COAL CONVERSION THAN LUMMUS RUNS

First-stage conversions of coal to THF solubles, calculated based on analyses of T-102 bottoms samples, average 91 ±1% for the samples from Run 242. This is in excellent agreement with the conversions to cresol solubles during "special product work-up periods" reported by Catalytic, Inc., which also averaged 91% (1). Each of the periods discussed above was operated at 860°F and 2400 psig (nominal). The SCT unit of the Lummus plant has been operated at conditions as mild as 830°F and 2000 psig, but has also been operated at the more severe conditions for a large part of the PDU program. THF conversions for those periods (850-860°F and 2400 psig), determined by Conoco, averaged 87% (7) for Runs SCT14 through SCT21 and 88% (7) for Runs 2SCT3 through 2SCT6. Lower severity conditions resulted in even lower coal conversions (5). Quinoline conversions, determined by Lummus, were typically 92% for the same periods (2). The greater first-stage conversion of coal to THF solubles, comparing Conoco's data for Run 242 and the PDU, is consistent with the greater SCT distillate yield reported by Rao, et al. (11) for Run 242 relative to the Lummus PDU and may reflect a greater SCT reaction severity during Run 242. The Lummus system has operated at coal space rates as low as 82 lbs/hr·ft^{3} (2SCT15-1014) but is more typically operated at coal

space rates of between 110 and 190 lbs/hr•ft³. Run 242 was consistently operated at about 92 lbs/hr•ft³ based on reactor volume and at about 44 lbs/hr•ft³ when the volume of the heated transfer line is included. The more severe first-stage conditions present during Run 242 as compared to typical PDU runs would be expected to affect SCT yields, thus changing the composition of the second-stage feed.

SECOND-STAGE CONVERSIONS AND CONVERSIONS ACTIVITIES

850°F$^+$ conversions during Run 242 were calculated based on Conoco's analyses as detailed in Reference 4. Average 850°F$^+$ conversions changed over the course of Run 242 in the following manner:

Date, 1982-83	Catalyst Age lbs SRC/lb Cat	T, °F	850°F$^+$ Conversion, % Average
12/01 - 12/14	72 - 204	679 - 685	13
12/15 - 12/17	216 - 242	699 - 704	16
12/18 - 01/04	253 - 467	718 - 721	16
01/08 - 01/21	520 - 685	745 - 750	21

It should be noted that these values average 5-7 absolute percentage points lower than the SRC conversions reported by Catalytic, Inc., (1) because of the different distillation procedures used (4).

At the end of Run 242, catalyst age was 500-700 lbs SRC/lb cat, H_2 partial pressure was 2500 psig, temperature was 750°F, the overall space velocity was 1 lb feed/lb cat•hr and the 850°F$^+$ space velocity was 0.6 lbs 850°F$^+$/lb cat•hr. At similar second-stage conditions the Lummus PDU typically obtains 30-35% 850°F$^+$ conversion. The comparison shown below is based on Conoco data.

Run	Period	Cat Age	T, °F	850°F$^+$ Conversion % Average ± Std Dev
242	1/8 - 1/21	520 - 685	745 - 750	21 ± 3
3LCF7	58 - 85	527 - 930	749 - 759	34 ± 3
3LCF8	27 - 49	299 - 526	732 - 751	33 + 2
3LCF9	0826 - 0122	697 - 1474	723 - 756	28 ± 6

The catalyst age units above are lb SRC/lb cat for Run 242 and lb 850°F$^+$/lb cat for the Lummus runs. The Run 242 catalyst age values should be increased by about 13% for an equal catalyst age comparison because of the difference in resid determinations (4). The closest comparison shown above in terms of catalyst age and temperature is for Runs 242 and 3LCF7. In that comparison, the average 850°F$^+$ conversion for Run 3LCF7 is four standard deviations greater than that for Run 242. Run 3LCF7 was made with a different Illinois basin coal (Indiana 5, Old Ben No. 1). Runs 242, 3LCF8 and 3LCF9 were all made with Illinois 6, Burning Star coal. Even though the data for Runs 3LCF8 and 9 shown above were obtained at generally lower temperatures than the data for Run 242, average 850°F$^+$ conversions are greater for the Lummus runs. Clearly the second-stage 850°F$^+$ conversion in Run 242 was lower than in typical Lummus runs at operating conditions (T, S.V., catalyst age, pressure, catalyst type, coal) that were ostensibly similar.

First order kinetic rate constants (k) and pre-exponential factors (A) were calculated for second-stage 850°F$^+$ conversion for Runs 242 (4) and 3LCF9 (5)

based on Conoco's analyses. Lummus uses an activation energy of 23,500 cal/mol for 850°F$^+$ conversion in the second stage (2). If it is assumed, for the sake of argument, that the activation energy is the same in the Wilsonville system, pre-exponential factors can be calculated to compare the resid conversion activities of the two systems. The data for Run 242 are compared to the data from Run 3LCF9 in Figure 1. It should be noted that the catalyst age units in Figure 1 are consistent. The catalyst ages of the Run 242 data, which were obtained from the report by Catalytic, Inc., (1) were increased by 13% to put them on a basis equivalent to the Run 3LCF9 data, i.e., on a lbs 850°F$^+$/lb cat basis. As shown in Figure 1, 850°F$^+$ conversion activity decreased with time for both runs as measured by the first-order pre-exponential factor. The data for Run 242 are consistently lower than the Run 3LCF9 data indicating that within the limits of the assumptions used in this model, 850°F$^+$ conversion activity was significantly lower in Run 242 than in Run 3LCF9.

There are several possible reasons for the difference in the calculated conversion activities in the two systems: 1) Simple first-order kinetics may not be a good description of the conversion reactions. Additionally, it may be more appropriate to use space velocity based on reactor volume rather than on catalyst weight for the resid conversion reaction since there may be a large thermal contribution to conversion. 2) The inherent reactivities of the feedstocks are almost certainly different. The clearly demonstrated differences in feed composition are expected to result in different reactivities. This could be caused in part by the different selectivities of the deashing processes as well as the different first-stage reaction severities. Batch experiments demonstrating different "thermal" reactivities of the feedstocks are described below in this paper. Different reactivities would require the use of different activation energies in the kinetic calculations. In fact, Catalytic, Inc., uses an activation energy value of 50,000 Btu/lb mol (27.8 kcal/mol) for Run 242 data(12) as opposed to the 23.5 kcal/mol used in our calculations. 3) One or both runs may have been operated with non-equilibrated solvent. 4) The use of the "effective" (average) temperature in the kinetic calculations for the Lummus system may give incorrect results because the LC-Finer operation is not strictly isothermal. Temperature differentials over the LC-Finer are often 50°F or greater (13).

YIELD DIFFERENCES CONSISTENT WITH CONVERSION DIFFERENCES

The greater first-stage severity and lower second-stage conversions of Run 242 in relation to Lummus Run 3LCF9 were discussed above. It would be expected that these differences would be reflected in the product yields of the two runs. A comparison of the yield structures of the two runs was reported by Rao, et al (11). The table below, based on those data, compares the net C_5^+ distillate yields by stage.

	Net C_5^+ Distillate Yield			
	Run 242		Run 3LCF9	
	As wt % MAF Coal	As % of Total Distillate Yield	As wt % MAF Coal	As % of Total Distillate Yield
First Stage	35.6	57	8.5	15
Second Stage	27.3	43	49.0	85
Total	62.9	100	57.5	100

Although total distillate yields are similar for the two runs, a much greater proportion of the distillate was produced in the first stage during Run 242. These results are consistent with conclusions drawn from our analyses of the runs.

THERMAL REACTIVITIES OF RUNS 3LCF9 AND 242 RESIDS

The comparison of Wilsonville Run 242 with typical Lummus operations described above showed that when second-stage samples were analyzed on an equivalent basis, the resid ($850°F^+$) conversion activity, as measured by the first-order kinetic pre-exponential factor, was lower in the Wilsonville system than the Lummus system. To examine the reactivities of the different feed resids, we performed a set of experiments to compare the "thermal" reactivities of the residual feeds to Lummus Run 3LCF9 and Wilsonville Run 242. One reason the compositions of the second-stage feed resids are different is the different deashing technologies in use at the two plants. Wilsonville uses CSD which selectively rejects preasphaltenes. In order to determine if the difference in reactivities (if any) of the second-stage feed resids were caused solely by deashing differences, we also tested a T-102 bottoms (first-stage product resid, non-deashed) sample from Run 242.

The conversion of resid in the second stage of ITSL is promoted by the distillate hydrogen donors in the solvent. Since the second stage of each plant is back-mixed, the product distillate better models the reactor inventory than the feed distillate. Therefore, the distillates used in this work were second-stage products whereas the resids were second-stage feeds.

The samples used for these experiments are described below:

3LCF9 Resid:	A composite sample of the $850°F^+$ resid fraction of LC-Finer feed samples from Run 3LCF9.
3LCF9 Distillate:	Same, but composited from the $850°F^-$ distillate products.
V-1064 Resid:	The residual ($850°F^+$) portion of the V-1064 (second-stage feed) sample from 1/13/83 of Run 242. A typical sample.
242 Distillate:	A composite sample of the $850°F^-$ distillate fraction of the V-1067 (second-stage product) samples from Run 242.
T-102 Bottoms:	The first-stage product resid from 12/19/82 of Run 242. A typical sample.

The method used for these experiments follows. The 30 ml microautoclave was charged with 9 g of the resid sample and 6 g of the distillate sample to be investigated. This approximates a "typical" resid/distillate ratio in the continuous units. The microautoclave vessel has heat-up and cool-down times of less than 2 min and is agitated vigorously to overcome mass transfer limitations. The vessel was charged with 1000 psig cold H_2 (<2300 psig at 750°F). Reactions were carried out for two hours at 750°F. 750°F was used because both continuous units were operated for some time at that temperature. Two hours is thought to approximate the average liquid residence times in the second-stages of the two continuous units. It is recognized that a batch microautoclave can only approximate the performance of the continuous unit; however, this work was done to obtain a comparison, not absolute reactivities. After each microautoclave run, the microautoclave contents were extracted with THF to separate the IOM and ash. The solubles were distilled to 320°C pot/270°C column/5 torr (850°F) using a microstill. Conversions and yields were determined from known feed and product compositions. Ash was assumed to carry through unchanged. $850°F^-$ was determined by difference and includes both distillate and total gas make. Each experiment was performed at least twice to obtain a measure (pooled standard deviation) of reproducibility. Each distillate sample was reacted with each resid sample at least in duplicate to determine the relative "thermal" reactivities of the resids and the effect of the distillates. The data are summarized in Table 1. As

shown in Table 1, the pooled standard deviation of our measurement of 850°F$^+$ conversion is 0.6% absolute.

No difference was observed that was dependent on the distillate solvent used in these tests even though there is a significant difference in their abilities to convert coal in a donor-only system (4, 5).

Unlike the distillate, the resids made a large, experimentally significant difference. About 15% of the resid from Run 3LCF9 converted to lighter materials, regardless of distillate. This compares to about 5 to 6% for the two Run 242 resids which did not react to significantly different extents from one another.

These results support the conclusion that the resid conversion activities calculated for Runs 3LCF9 and 242 were different, at least in part, because of a difference in the reactivities of the feedstocks. The results indicate that the lower resid conversions obtained in Run 242 as compared to Run 3LCF9 during periods of generally comparable operating conditions resulted at least partly from a less reactive second-stage feedstock. This is consistent with the first-stage distillate yields in Run 242 being higher than in Run 3LCF9 (12), thus leaving only the more refractory materials for second-stage conversion.

SUMMARY

- The compositions and relative proportions of both the 850°F$^-$ distillate and 850°F$^+$ resid fractions in the process streams were fairly constant in Wilsonville Run 242.

- The Critical Solvent Deashing (CSD) unit selectively rejected preasphaltenes during Run 242. The reduced level of preasphaltenes thus fed to the hydrotreater could affect hydrotreater performance.

- The characteristics of the process oils from Run 242 are significantly different from the characteristics of the corresponding process oils from Lummus PDU operations, although both operations were conducted in the ITSL mode. For many measured parameters, the data from Run 242 and the Lummus operations do not share a common range. Much of the difference may be ascribed to differences in the first-stage (thermal) severities and to selectivities of the deashing operation between the Lummus and Wilsonville operations. Characteristics of the start-up solvents may also have influenced this comparison.

- First-stage coal conversions to THF solubles averaged 91% for Run 242. This is 3 to 4% absolute greater than the THF conversions calculated for Lummus PDU runs operated at similar temperature and pressure conditions and is consistent with the generally lower first-stage space velocity used in Run 242. The more severe first stage conditions used in Run 242 may be one reason for the different first-stage yields and different second-stage feed compositions in that run as compared to PDU operations.

- Second-stage 850°F$^+$ conversions in Run 242 were clearly lower than in typical PDU runs at operating conditions that were ostensibly similar. A possible reason for this is the dissimilar second-stage feed composition, again partially a result of the deashing process and first-stage severity differences.

- A statistically-designed set of experiments showed that the second-stage residual feed from Wilsonville Run 242 was significantly less reactive than the corresponding material from Lummus Run 3LCF9 at thermal/donor, i.e., non-catalytic conditions. This is consistent with the analytical results.

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TABLE 1

THERMAL REACTIVITIES OF RUNS 3LCF9 AND 242 RESIDS
SUMMARY OF RESULTS

Samples		850°F$^+$ Conversions, wt %			
Distillate	Resid	Trial 1	Trial 2	Trial 3	Average
3LCF9	3LCF9	15.8	14.4	-	15.1
	V-1064	5.6	6.4	-	6.0
	T-102 Bottoms	5.1	5.8	-	5.4
242	3LCF9	15.6	15.4	-	15.5
	V-1064	4.8	4.0	4.9	4.6
	T-102 Bottoms	6.8	5.8	-	6.3

Pooled standard deviation = 0.6% absolute

Average conversion using 3LCF9 distillate = 8.8%
Average conversion using 242 distillate = 8.8%
} No significant difference

Average conversion using 3LCF9 resid = 15.3%
Average conversion using V-1064 resid = 5.3%
Average conversion using T-102 bottoms resid = 5.9%
} 3LCF9 resid more reactive than either 242 resid

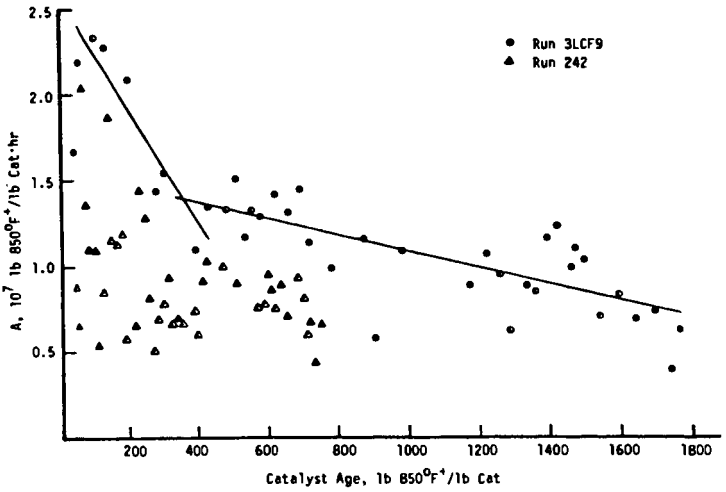

Figure 1. Comparison of First-Order Pre-Exponential Factors vs Catalyst Age. Runs 242 and 3LCF9.